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On-Site GC/MS Analysis of Chapman Gasification Separator Liquor

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16. ABSTRACT The report gives results of a characterization of a wastewater stream from a coal gasification plant, using on-site extraction and GC/MS analysis. Extractable material in the wastewater was primarily phenols and alkylphenols, accounting for about 99% of the total mass identified. Several polynuclear aromatic compounds were also identified. The composition of the sample deteriorated even though the water was held in amber bottles at 4 C: this was most evident in the concentration of dimethylphenols which dropped about 75% during 2 weeks of refrigerated storage. Ambient sample storage produced a greater decrease in the concentration of phenol, but did not appear to affect the alkylphenols or the base/neutral compounds as much. The observed changes in composition should hamper any off-site wastewater treatability studies with waters of this type. Diisopropyl ether (DIPE) extraction confirmed the 99-plus% removal efficiency of phenol which had been demonstrated in previous studies. Wet oxidation removed organics almost as efficiently as DIPE extraction, but may have limited use because of its high operating cost.

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Analyzing		GC/MS Analysis	14B
Waste Water	Gas Chromatography	Diisopropyl Ether Extraction	07D
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ABSTRACT

This report presents the results of a study to characterize a wastewater stream from a coal gasification facility using on-site extraction and GC/MS analysis. The objectives of this program were to:

- Characterize the wastewater organic components primarily for selected Priority Pollutants, Appendix C and synfuels compounds,
- Investigate the stability of these compounds under refrigeration and ambient storage, and
- Evaluate the removal of organics by diisopropyl ether extraction and wet oxidation.

Extractable material in the wastewater consisted primarily of phenols and alkylphenols. These compounds account for about 99 percent of the total mass identified. Several polynuclear aromatic (PNA) compounds were also identified. Deterioration in the composition of the sample was observed even though the water was held in amber bottles at 4°C. This was most evident in the concentration of dimethylphenols which dropped approximately 75 percent during two weeks of refrigerated storage. Ambient sample storage produced a greater decrease in the concentration of phenol but did not appear to affect the alkylphenols or the base/neutral compounds as much. It is expected that the observed changes in composition would hamper any off-site wastewater treatability studies with waters of this type. The diisopropyl ether (DIPE) extraction confirmed the 99+ percent removal efficiency of phenol which had been demonstrated in previous studies. Wet oxidation removed organics almost as efficiently as DIPE extraction but may have limited use due to the high cost of operation.

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GLOSSARY OF ACRONYMS

ABN	Acid-base/neutral
B/N	Base/neutral
BTX	Benzene/toluene/xylene
DFTPP	Decafluorotriphenylphosphate
DIPE	Diisopropyl ether
DMP	Dimethylphenol
2,4-DMP	2,4-Dimethylphenol
EPA	Environmental Protection Agency
FID	Flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GRAV	Gravimetric analysis of solvent extractable residue after evaporation
HP-5993B	Hewlett-Packard gas chromatograph/mass spectrometer model number 5993B
PNA	Polynuclear aromatic
TCO	Total chromatographable organics

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SECTION 1

INTRODUCTION

Radian Corporation has been conducting environmental assessment studies of low and medium-Btu coal conversion facilities under contract to the Environmental Protection Agency during the past five years. A Chapman-Wilputte gasification facility was the first source characterized in such an assessment. This plant is in continuous operation and since it is located within the U. S., it provides an easily accessible source of coal gasification wastewater. Three previous studies have also examined this water as part of an environmental data base for coal conversion technologies to provide input to the planning and design of future gasification facilities and formulation of guidance for water discharges. The program described in this report was designed to characterize the separator liquor and aqueous process condensate from the plant under conditions which would minimize any sample deterioration thus providing a more accurate determination of the composition of the waste stream.

1.1 Objectives

The primary objectives of this program were:

- Characterization of the separator liquor. This included sampling over a 100-hour monitoring period to determine the average composition and range of variability of the identified compounds.
- Determination of sample stability by monitoring one sample for a month for deterioration of identified compounds.
- Investigate methods for reducing the levels of organic materials in the wastewater by wet oxidation and diisopropyl ether (DIPE) extraction.

In addition to these objectives, the feasibility and utility of the operation of a GC/MS system installed in a mobile laboratory designed for field use was evaluated.

1.2 Summary of Results

This Mobile GC/MS program provided a more representative characterization of the separator liquor than had been previously achieved.

EPA Priority Pollutant Appendix A base/neutral, acid extractable and volatile organic compounds, Appendix C compounds and 57 organic species of environmental interest were quantitated. Of these, the Appendix A volatile organic compounds (purgeable halocarbons and aromatics), the Appendix C compounds and the 57 additional organics had not been quantitated during previous studies. Phenolic compounds appear to represent essentially all of the total chromatographable organic (TCO) material in the acid fractions and a major portion of material in the base/neutral fractions.

Using a methylene chloride/diethyl ether extraction procedure, it was observed that a high percentage of the phenolic compounds (usually found only in the acid fraction) were extracted into the base/neutral fraction. Therefore, in order to determine the concentrations of phenolic compounds in the separator liquor, both the acid and base/neutral fractions were analyzed and the values for phenolic compound concentrations in each fraction were added to give the value for total phenolic compound concentration.

Data resulting from daily analyses of the separator liquor show high variability in all species determined. Although the number of data points is insufficient for a statistical treatment of the results, comparisons between these data and that previously reported indicate definite trends. A conclusion may be drawn that extraction and analysis of the separator liquor immediately after sampling results in higher concentrations of the species determined than off-site extraction and analysis after some time delay. In addition, the stability studies indicate that many of the species determined degrade with time even with storage at 4°C in amber glass bottles. The data, therefore, suggest that the higher concentrations of organic species measured immediately after sampling are more representative of the actual separator liquor composition even with the high degree of variability in the results.

Results obtained from this program confirm the 99 percent removal efficiency of phenols by diisopropyl ether extraction found in previous work and also show a 90 percent removal efficiency of phenol and alkylphenols by wet oxidation. Wet oxidation demonstrated a potential advantage over biological treatment of wastewater in that it is capable of reducing the levels of many organic compounds which are resistant or moderately resistant to biodegradation. Wet oxidation may not be economically feasible on an industry wide basis, but has been used in a few applications.

Information contained in this report related to the suspected degradation should serve as a guide for future wastewater characterization and treatability efforts on waters of this type. The formation of higher molecular weight refractory organic compounds which could present significant treatability problems is suggested by the apparent decrease in the concentration of phenolic compounds coupled with no decrease in the concentration of total extractable organics (TCO and GRAV). These data should also provide information as to the species of organic compounds which could possibly be present in the sludge and/or air emissions from water treatment systems.

1.3 Recommendations

The recommendations presented below are given for two major categories:

- Analytical methodologies.
- Additional studies which would provide complementary data to this study.

Analytical Methodologies

Recommendations for analytical methodologies are presented with regard to some of the difficulties encountered during sample analysis and data reduction.

The major analytical difficulty encountered was associated with the extraction of the phenols into the base/neutral fraction. Due to the high concentration of phenolic compounds, a better partitioning of acid and base/neutral compounds is required. This might be achieved by:

- An acid/neutral followed by a basic extraction, then separation of acid and neutral compounds,
- A less vigorous extraction of base/neutral compounds, using only methylene chloride for the base/neutral compounds, but continuing with methylene chloride/diethyl ether extraction for the acidic compounds.

For each suggested procedure modification, extraction efficiencies must be determined by performing the separation procedure with controls consisting of known quantities of standard compounds added to samples of the separator liquor as well as water blanks.

The procedure for analysis of a sample of this complexity should be refined to provide a more cost effective approach. The necessity of using GC/MS for every analysis has not been established; these analyses might be performed as accurately with a gas chromatograph equipped with a flame ionization detector and capillary column. The capillary column would provide better separation and detection of the compounds than packed columns. Once retention times are determined adequately for compounds of interest, GC will be more cost effective than GC/MS. Periodic confirmation of compound identifications by GC/MS would still be required.

Future studies should also incorporate an experimental determination and documentation of the variability associated with the sampling and analytical procedures as well as a determination of what effect this variability has on the results.

The necessity of on-site extraction and analysis versus on-site extraction followed by off-site analysis should also be investigated. The stability of the extracted samples should be evaluated by analysis of the extract immediately after extraction and at predetermined intervals following the extraction in order to monitor any decrease in the concentration of one or more compounds. If the stability of extracted samples is adequate to allow transport and storage, the expense of providing on-site analytical capabilities could be avoided.

Additional Studies

During this program the separator liquor from the plant was characterized for organic content

- immediately following collection,
- periodically over a period of one month under refrigerated storage,
- after a period of 3 weeks at room temperature storage,
- following DIPE extraction performed immediately after collection, and
- following wet oxidation performed immediately after collection.

Additional studies which characterized the wastewater after biological treatment would supplement the information already obtained. A more complete set of data would then be available when water treatment information is required for selection of treatment schemes for wastewater streams of similar composition.

The use of a capillary column is recommended to provide sufficient separation of the complex isomeric mixtures contained in the separator liquor. The separation provided by the packed columns used was not sufficient to permit the data interpretation software to distinguish the quantitating ions for each of these isomers. Consequently, extensive manual data interpretation was required. If adequate separation of the isomers could be achieved, as with a capillary column, then the software package should be able to function as designed, providing identification and quantitation of compounds in a short amount of time.

SECTION 2

PLANT DESCRIPTION

The Chapman facility under examination produces a low-Btu gas which is used as fuel for process heaters. The facility is equipped with 12 operational Chapman gasifiers. However, at the time this study was conducted, fuel demands were low and could be met by operating two gasifiers at any given time.

A block flow diagram of the Chapman facility is given in Figure 2-1. The point at which liquor samples were obtained is indicated in this figure.

Three operations are conducted at the Chapman facility: coal handling, gasification, and gas purification (particulate removal and gas quenching and scrubbing). The operations consist of one or more discrete steps, as follows:

- Coal handling - Consists of delivery and storage of pre-sized coal in hopper cars, along with conveying and storing this coal in the gasifier feed hoppers.

- Coal gasification - Consists of producing raw, low-Btu gas from coal using fixed-bed, atmospheric pressure, single-stage Chapman gasifiers. The coal enters the gasifier through a rotating feeder (barrel valve) and is spread across the bed by a distribution arm. The coal is then reacted with a steam/air mixture to produce a hot (840 to 950 K, 1,050 to 1,250°F) low-Btu gas. Ash is collected in a water-sealed ash pan and removed by an ash plow. Pokeholes located on top of the gasifier are opened periodically to permit the insertion of rods to break up any coal agglomerates that form in the gasifier.

Gas Quenching and Scrubbing

The hot gas leaving the cyclones is quenched by spraying water into the exit lines from each cyclone. Excess quench water is collected in a liquor trap (one trap for each gasifier/cyclone), while the cooled gas from all operating gasifiers enters a collecting main. Water sprayed inside this main further cools the gas to approximately 340 K (150°F). Tar and quench liquor from the liquor traps and the collecting main are sent to

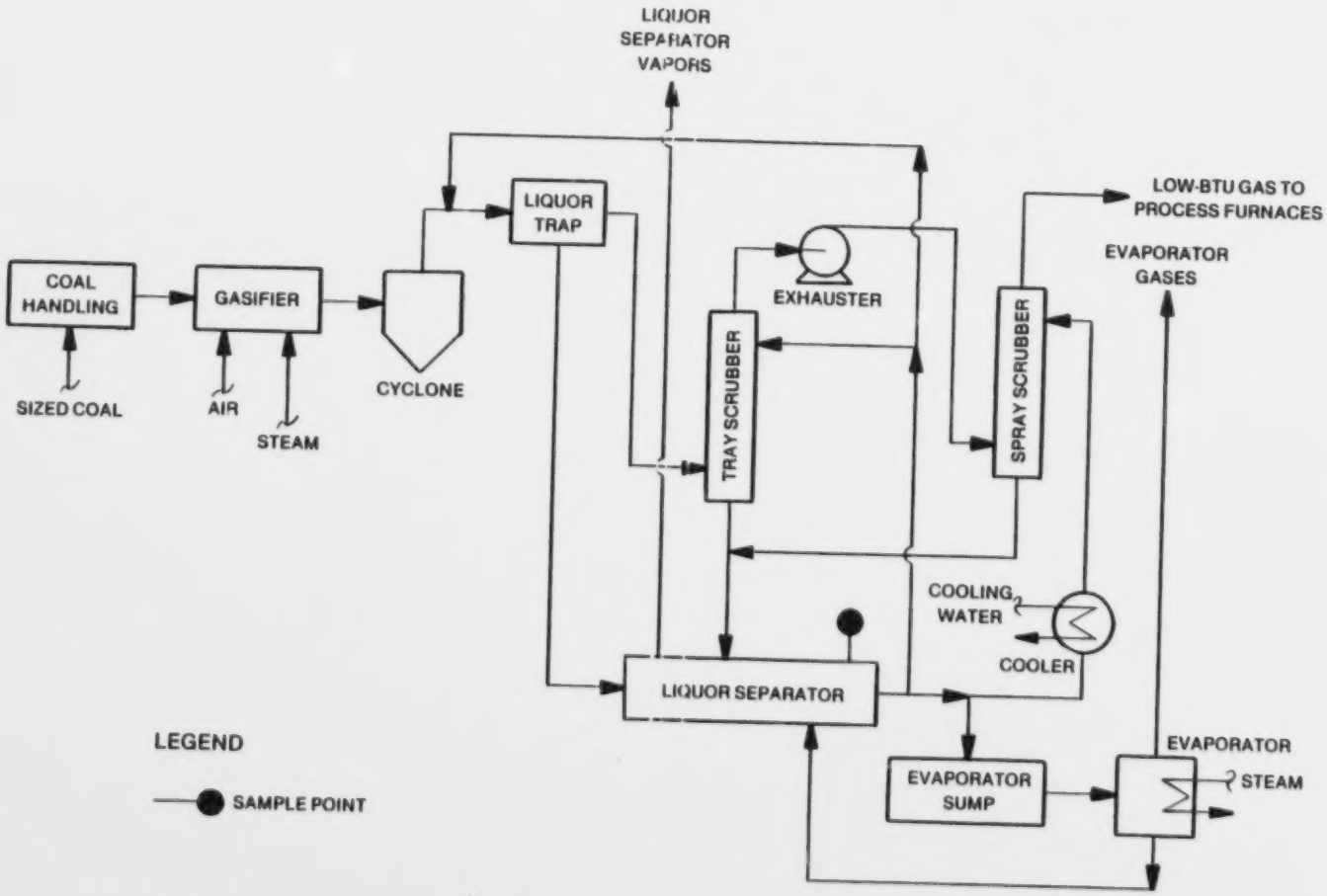

Figure 2-1. Simplified Process Flow Diagram for the Chapman Facility Showing Sampling Point

the liquor separator. Pitch (a lighter-than-water, tarry material) and agglomerated particulates which accumulate in the liquor traps are collected for periodic incineration.

After the initial quenching step, the gas is cooled further by water in two tray scrubbers which are operated in parallel. Here, most of the tars, oils, and particulates are scrubbed from the gas as it is cooled to approximately 330 K (135°F).

The gases exiting the tray scrubbers are recombined and compressed before entering a spray scrubber. In the spray scrubber, some residual tars, oils, and particulates are removed as the gas is further cooled to about 320 K (120°F). The effluent scrubbing liquor from both the spray and tray scrubbers is sent to the liquor separator.

Liquor Separator

The liquor separator at the Chapman facility is a large concrete tank (5 x 12 x 2 meters; 16 x 40 x 6 feet). Process condensate and condensed tars and oils from the quenching/scrubbing steps enter at one end of the tank. Turbulence caused by the incoming liquor is minimized by a series of 5 baffles in the tank. The tars and oils settle to the bottom of the separator and are removed periodically for use as an auxiliary fuel in a coal-fired boiler. A portion of decanted water from the liquor separator is cooled in indirect heat exchangers before being reused in the spray scrubber. The remainder of the water is recirculated to the other quenching and scrubbing steps.

Water Treatment

Water treatment problems are minimized at this gasification facility by operating the gasification process so that there is minimal accumulation of water. If excess aqueous process condensate accumulates, it is evaporated using steam. The resulting brine is recycled to the separator. Any excess dissolved solids precipitate and are ultimately removed with the tar and oil.

2.1 Plant Operation

The Chapman coal gasification facility operates 24 hours per day with a production rate determined by the fuel demand of the process heaters in an adjacent building. A single gasifier is capable of producing gas at a rate that will fire a minimum of two and a maximum of four heaters. During Radian's tests, process heaters were fired by gas from two gasifiers.

The product gas exit temperature, the saturation temperature of the gasifier inlet air, and product gas flow rate were monitored with instrumentation installed on the gasifiers. The values for these parameters

were recorded for each day of sampling and are presented in Table 2-1. The pH and temperature of the separator liquor was measured at the time of sampling with a pH meter and thermometer by Radian. These data are given in Table 2-2.

TABLE 2-1. GASIFIER OPERATING CONDITIONS DURING SAMPLING PERIOD

Date	Saturation* Temperature	Gas Flow $Nm^3/hr.$	Gas Temperature
09/05/80	336 K	2550 - 2690	852 K
09/06/80	336 K	2550	852 K
09/07/80	336 K	2550	852 K
09/08/80	336 K	2550	866 K
09/09/80	336 K	3440	880 K
09/13/80		3680 - 3960	

*Dewpoint of the inlet air

TABLE 2-2. PHYSICAL DATA FOR SEPARATOR LIQUOR DURING SAMPLE COLLECTION

Date/Time	pH	Temperature
09/05/80 - 1045	7.2	332 K
09/06/80 - 0945	6.6	334 K
09/07/80 - 1000	6.7	332 K
09/08/80 - 0900	6.7	331 K
09/09/80 - 0900	6.6	332 K
09/13/80 - 1415	6.9	332 K

SECTION 3

METHODOLOGIES

3.1 Sampling Methodology

Water samples were collected through an opening on top of the separator liquor tank. A bucket was used to collect the aqueous phase from the tank at a point adjacent to the final overflow baffle. After the sample was taken, the pH and temperature of the water were measured and the sample was then taken immediately to the mobile laboratory for extraction. Samples were also collected immediately prior to the diisopropyl ether extraction and wet oxidation work.

3.2 Analytical Methodology

Samples of separator liquor were analyzed to determine the concentration of organic species which were judged to be of environmental significance. Table 3-1 presents a listing of the compounds which were selected. These compounds were selected for analysis based on their concerns in several areas. The Priority Pollutant Appendix A and Appendix C compounds are of interest due to their regulatory significance, however, some halogenated compounds, pesticides, and PCB's which had a low probability of occurrence were not included. An additional group of compounds was included based on their documented behavior in biological oxidation systems. Still others were included based on their known and/or suspected carcinogenic activity and their probability of occurrence in coal conversion processes. The compounds from this list which are not included in the data tables presented in Section 4 can generally be assumed to be not detected at less than 5 ppm for the base/neutral extractable compounds and 1 ppm for the acid extractable compounds. The "less than" values are given in the tables for compounds present at less than the minimum detectable limit in the analyzed extract.

The procedures used for the extraction and analysis of the separator liquor are outlined in the following subsections. These subsections also include additional procedures which were followed during the wastewater treatment studies.

3.2.1 Extraction Procedure

Extraction of the separator liquor was begun immediately upon receipt of the sample. The liquor was prepared for GC/MS analysis using a modified EPA acid/base extraction procedure (Ref. 1). Before the extractions, two 40 mL aliquots of liquor were taken for volatile organic compound analysis, then 100 mL of the water was spiked with pentafluorophenol and d_8-naphthalene to yield concentrations of 10 ppm (in the water)

TABLE 3-1. COMPOUNDS OF ENVIRONMENTAL INTEREST FOR MOBILE GC/MS PROGRAM

BASE/NEUTRAL EXCTRACTABLE COMPOUNDS

1,3-Dichlorobenzene	Butyl benzyl phthalate
1,4-Dichlorobenzene	Bis(2-ethylhexyl)phthalate
Hexachloroethane	Chrysene
1,2-Dichlorobenzene	Benz(a)anthracene
Bis(2-chloroethyl)ether	3,3-Dichlorobenzidine
Bis(2-chloroisopropyl)ether	Di-n-octyl phthalate
Nitrobenzene	Benzo(b)fluoranthene
N-Nitrosodimethylamine	Benzo(k)fluoranthene
N-Nitrosodi-n-propylamine	Benzo(a)pyrene
Hexachlorobutadiene	Indeno(1,2:C,D)pyrene
Isophorone	Benzo(a,h)anthracene
1,2,4-Trichlorobenzene	Benzo(g,h,i)perylene
Bis(2-chloroethoxy)methane	Pyridine
Naphthalene	2-Ethylthiophene
Hexachlorocyclopentadiene	Cumene
2-Chloronaphthalene	2-Ethylpyridine
Acenaphthylene	Indan
Acenaphthene	4-Ethylpyridine
Dimethyl phthalate	Camphor
2,6-Dinitrotoluene	1-Methylnaphthalene
4-Chlorophenyl phenyl ether	Quinoline
Fluorene	2-Methylquinoline
2,4-Dinitrotoluene	2,3-Dimethylnaphthalene
Diethyl phthalate	Diphenylether
N-Nitrosodiphenylamine	Indole
1,2-Diphenyl hydrazine	2,6-Dimethylnaphthalene
Hexachlorobenzene	4-Methylquinoline
4-Bromophenyl phenyl ether	3-Methylindole
Phenanthrene	2-Methylindole
Anthracene	Diphenylamine
Di-n-butyl phthalate	1-Phenylnaphthalene
Fluoranthene	Triphenylene
Pyrene	Perylene
Benzidine	Diethylamine
Dimethylamine	Dibutylamine
Thiophene	Coronene
3-Methylthiophene	Dibenzofuran
Quinaldine	Dibenzothiophene
Lepidine	

(Continued)

TABLE 3-1 (CONTINUED)

ACID EXTRACTABLE COMPOUNDS

2-Chlorophenol	2,3-Dimethylphenol
2-Nitrophenol	2,3,5-Trimethylphenol
Phenol	2-Isopropylphenol
2,4-Dimethylphenol	3,4-Dimethylphenol
2,4-Dichlorophenol	2-Ethylphenol
2,4,6-Trichlorophenol	3-Ethylphenol
p-Chloro-m-cresol	3,5-Dimethylphenol
2,4-Dinitrophenol	2-s-Butylphenol
4,6-Dinitro-o-cresol	2,5-Dimethylphenol
Pentachlorophenol	3-Isopropylphenol
4-Nitrophenol	2,4,6-Trimethylphenol
Camphor	Indanol
α-Terpineol	3-Hydroxybenzaldehyde
2,6-Dimethylphenol	2-Methyl-1-naphthol
2-Methylphenol	1-Naphthol
3-Methylphenol	4-Hydroxybenzaldehyde
4-Methylphenol	2-Naphthol
2-Ethylphenol	Resorcinol
Catechol	9-Phenanthrol

VOLATILE ORGANIC COMPOUNDS

Bis(chloromethyl)ether	Benzene
Carbon tetrachloride	Chlorobenzene
1,2-Dichloroethane	1,1,1-Trichloroethane
1,1-Dichloroethane	1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane	Chloroform
1,1-Dichloroethylene	1,2-Trans-dichloroethylene
1,2-Dichloropropane	1,2-Dichloropropylene
Ethylbenzene	Methylene chloride
Bromoform	Dichlorobromomethane
Trichlorofluoromethane	Chlorodibromomethane
Tetrachloroethylene	Toluene
Trichloroethylene	2-Chloroethyl vinyl ether
o-Xylene	m-Xylene
p-Xylene	Styrene
Methyl ethyl ketone	Hexanoic acid

of each compound. To extract the base/neutral extractable compounds, the pH of the water was adjusted to pH $\geq$12 with 6N NaOH and extracted twice with two consecutive aliquots of 100 mL of methylene chloride, then with two consecutive aliquots of 100 mL diethyl ether. The large volume of solvent was used in order to minimize the amount of emulsion formed during extraction. The water was then acidified to pH $\leq$2 to obtain the acid extractable compounds and extracted twice with 100 mL aliquots of methylene chloride followed by similar extractions with diethyl ether. The methylene chloride and ether extracts were combined according to pH and dried over anhydrous sodium sulfate. Extracts were concentrated to 10 mL using a Kuderna-Danish concentrator equipped with a 3-ball Snyder column and sealed in screw cap vials with Teflon®-faced septa. A 1:100 dilution of the acid extract was also made and submitted for analysis.

3.2.2 GC/MS Analysis

The sample extracts were analyzed on-site for volatile organic and acid extractable compounds using a Hewlett-Packard 5993B GC/MS system. A portion of the base/neutral extracts were analyzed in-house due to instrument (GC column) difficulties and time limitations while in the field. Samples were analyzed according to EPA procedures (Ref. 2) for Priority Pollutants as well as other compounds of environmental interest.

The concentrated extracts were analyzed for acid and base/neutral extractables by direct injection and for volatile organic species by the purge and trap method (Ref. 2). The operating conditions for each class of compounds were:

Acid Extractable Compounds:

Column:	1.8 m x 2 mm i.d. SP-1240 DA on 100/120 Supelcoport
Oven Program:	323 K to 473 K at 10°/min.
Column Flow:	Helium at 25 mL/min.
Mass Range:	45 amu to 300 amu.
Scan Rate:	2 sec./scan.

Base/Neutral Extractable Compounds:

Column:	1.8 m x 2 mm i.d. SP-2250 DB on 100/120 Supelcoport
Oven Program:	323 K to 533 K at 8°/min. Initial Hold = 4 min.
Column Flow:	Helium at 20 mL/min.
Mass Range:	45 amu to 300 amu.
Scan Rate:	2 sec./scan.

Volatile Organic Compounds:

Column:	2.4 m x 2 mm i.d. SP-1000 on Carbopak B
Oven Program:	343 K to 493 K at 10°/min.
Column Flow:	Helium at 20 mL/min.
Mass Range:	45 amu to 300 amu.

The Hewlett-Packard 5993B has the capability of using a computer program to determine day to day instrument variations as well as a manual program employed to adjust these parameters. It also has the capability of normalizing files so that a standard of decafluorotriphenylphosphate (DFTPP) meets the EPA ion abundance criteria for that spectra. Both of these features were employed in the data processing of all compounds. Searches were done manually and identified compounds were quantitated against standard mixtures which had either been obtained commercially or prepared at Radian. Quantification was done by response factor comparison to a known amount of internal stanadard, d_{10}-anthracene for the extractable compounds and 2,4-dichlorobutane for the volatile organics.

3.2.3 Diisopropyl Ether (DIPE) Extractions

A 1.5 liter grab sample of the separator liquor was first extracted three times with 450 mL of diisopropyl ether. This extraction scheme was designed to have the same number of theoretical stages (2.6) as the Lurgi Phenosolvan process. The extracted water was then purged with a stream of zero helium (helium containing <2 ppm total hydrocarbons) in a darkened room to remove any residual solvent. A 50 mL aliquot of the DIPE extracted water was then base/netural and acid extracted according to the procedure in Section 3.2.1 using adjusted solvent volumes and analyzed by GC/MS.

3.2.4 Wet Oxidation

A 500 mL aliquot of the raw wastewater was measured into a one liter stainless steel high pressure bomb. The bomb was then heated to a temperature of 533 K (500°F) and simultaneously pressurized to 1.03E7 Pa (1,500 psig) using zero air (air containing <2 ppm total hydrocarbons) (see Figure 3-1). It remained under these conditions for approximately 30 minutes. After the bomb was cooled and then depressurized, the water was decanted from the resulting solids and immediately extracted.

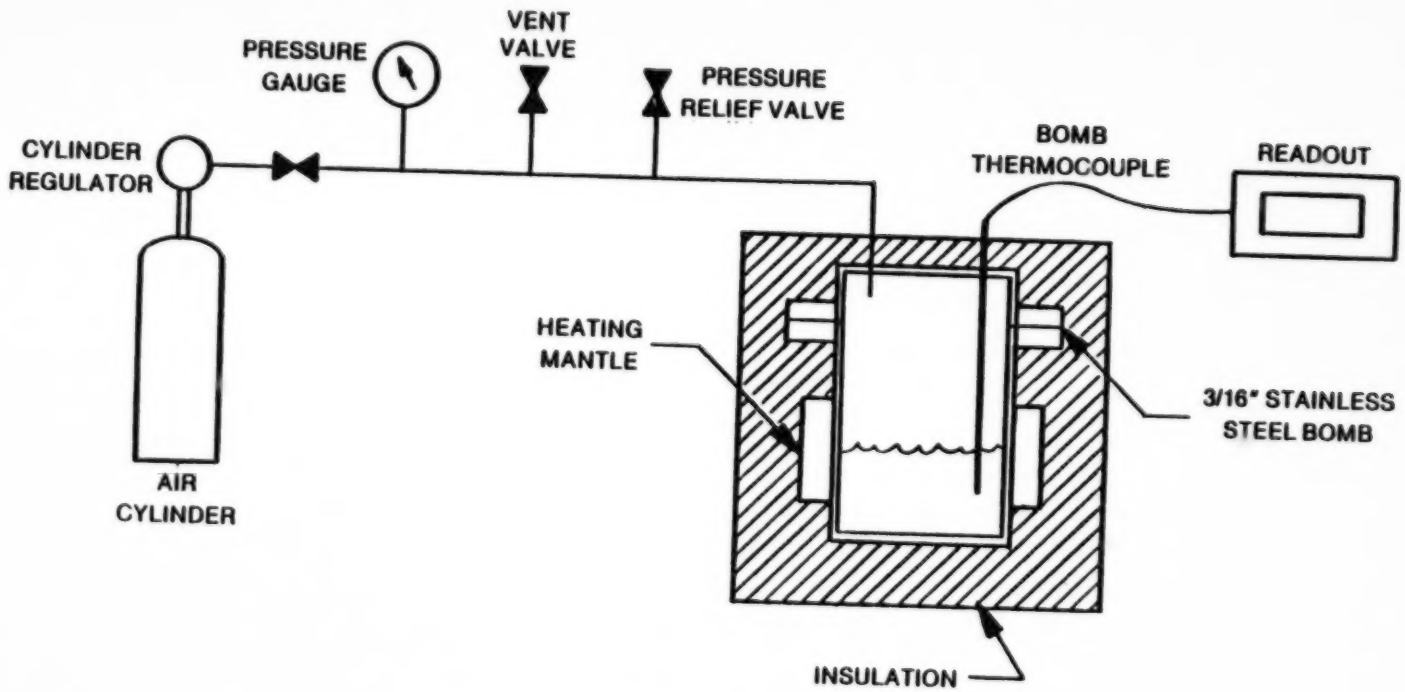

Figure 3-1. Schematic of the Wet Oxidation Apparatus

SECTION 4

RESULTS

Organic components in the separator liquor were quantitated on-site using a GC/MS installed in a mobile field laboratory. The variability of separator liquor composition was determined over a 100-hour monitoring period. Sample stability was investigated by sequential analysis during both refrigerated and ambient storage of a sample. Removal of organics by wet oxidation and extraction with diisopropyl ether was evaluated.

4.1 Characterization of the Separator Liquor

The 100-hour monitoring period provided five sets of data characterizing the separator liquor. An additional data set was generated by the water treatment study. All six sets were included in the determination of average concentration of each compound which was identified.

GC/MS analysis has identified 40 percent to 100 percent of the total extractable material as determined by the sum of the total chromatographable organics (TCO) and gravimetric analysis of residue after evaporation (GRAV). Of the identified compounds, the phenolics account for about 99 percent of the total mass. Methylphenols contribute the majority of the material identified; with phenol the next largest contributor. Of the base/ neutrals, the compounds present in the greatest concentrations are the indoles, followed by the naphthalenes. The volatile organic compounds were identified at concentrations generally 2 to 4 orders of magnitude lower than the extractable compounds.

A further discussion of these data are presented in the following subsections.

4.1.1 Sources of Variability

Significant variability is evident in the data obtained for extractable organics from the six sets of samples. This data population is insufficient for meaningful statistical analysis. The program design did not include provisions for separation and quantitation of the three major possible sources of variability: process variations, sample collection, and analysis. Variability in the process was assumed to be negligible since the residence volume of the separator is large enough to dampen the effects of a major short term variation in the inlet liquor composition on the total liquor composition.

The sample collection technique was very simple, so the variability introduced during collection should be small. However, the inclusion of relatively small quantities of separable organic materials in the sample would have a large impact on the organic content of the samples. The reproducibility of the TCO and GRAV results for total extractable organics support the assumptions that process and sampling variabilities are relatively small contributors to the total variability.

Analytical variability in the GC/MS analysis has been documented by previous studies such as "round robin" programs (Ref. 3) and Radian in-house QA programs (Ref. 4). The relative error for samples spiked with priority pollutants in the "round robin" study was about 25 percent. The relative error for samples spiked with phenol during in-house programs was about 80 percent. Results from these programs at least give an indication of the analytical variability which is associated with the GC/MS analysis itself. Additional variability was also introduced due to the extraction of acid extractable compounds into the base/neutral fraction. The acid extractables in the base/neutral fraction were determined under base/neutral chromatographic conditions. The quantitation of these compounds is subject to a greater amount of error since the chromatography was not optimized for acid extractable compounds.

4.1.2 Acid Extractable Compounds

Table 4-1 presents the average concentrations for each acid extractable compound detected. The range of concentrations given is the minimum and maximum values determined for each species during six days of monitoring. The detailed results from which these averages and ranges are derived are presented in Appendix A. With the exception of the methylphenols, the number of identifications represents the number of samples (out of a total of six) which contained the compound. TCO and GRAV data are also presented to give an indication of the gross amount of extractable material present. TCO's were done on only three samples. The TCO and GRAV values are representative of the acid extract itself with no adjustment to compensate for acid extractable compounds identified in the base/neutral fraction. The concentrations given for each species represented the total amount of that compound present in both the acid and base/neutral extracts.

The total average amount of extractable phenolic material is 6,900 mg/L, of this, approximately 35 percent is phenol, 47 percent is methylphenols, and 18 percent is dimethylphenols.

During the analysis of the acid and base/neutral extracts, it was observed that a significant portion of the phenolics had been extracted into the base/neutral fraction. The results in Table 4-1 are the totals from both the acid and base/neutral fractions. This carryover was much greater for the methyl- and dimethylphenols than it was for phenol itself. The base/neutral fraction contained an average of 20 percent of the total

TABLE 4-1. GC/MS ANALYSIS RESULTS OF EXTRACTED SEPARATOR LIQUOR ACID EXTRACTABLE COMPOUNDS

Identifications/ Compound	Concentration in the Liquor (mg/L) Average	Range	# of Determinations
**TCO	2500	2100 - 2700	3/3
GRAV	5400*	3900 - 6900	6/6
† Phenol	2400	1900 - 3400	6/6
Methylphenols	3200*	1500 - 4700	6/6
+ Dimethylphenols(total)	1200	330 - 1900	6/6
†♦2,4-Dimethylphenol	420	98 - 820	6/6
Trimethylphenol	0.82	0.35 - 2.2	6/6
Indanol	1.7	<0.07 - 3.2	6/6
1-Naphthol	5.0	3.3 - 8.5	5/6
2-Naphthol	6.7	5.4 - 9.2	4/6
Resorcinol/Catechol	30	3.6 - 65	5/6
Hydroxybenzaldehyde	5.7	<0.18 - 19	6/6

†Appendix A Priority Pollutants.

*One data point not included in the average was rejected due to extremely high value, but compound was identified 6 of 6 times.

♦The portion of 2,4-DMP from the B/N fraction was estimated from the amount found in the acid fraction. The value presented here represents the sum of the acid and B/N fractions.

+Includes 2,4-DMP.

**TCO and GRAV values represent only the acid extract. Concentrations given for each compound represent the total amount of the compound present in both the acid and neutral extracts.

reported phenols, 53 percent of the methylphenols and 82 percent of the dimethylphenols. Table A-1 in the Appendix shows the actual amount of carry- over for each compound in each sample. The presence of phenolic compounds in the base/neutral fraction could be attributed to the relatively high concentration of phenolic compounds and the use of diethyl ether in the extraction procedure. The diethyl ether provided a polar organic medium (solvent) which favored the dissolution of the polar phenolic compounds in spite of the high pH of the water.

When the base/neutral extracts were analyzed for carryover, the dimethylphenols were not speciated. Since 2,4-dimethylphenol is a priority pollutant and, therefore, is a compound of high interest, an estimate was made of the total concentration of this compound. The total was estimated by determining the percentage of 2,4-dimethylphenol (2,4-DMP) in the total amount of dimethylphenols (DMP) found in the acid extract. This percentage was then applied to the total DMP concentration found in the base/neutral extract to estimate the concentration of 2,4-DMP in the base/neutral extract. The concentration of 2,4-DMP in the acid extract and the estimated concentration of 2,4-DMP in the base/neutral extract were then added together for the total reported concentration of 2,4-dimethylphenol.

4.1.3 Base/Neutral Extractable Compounds

The average concentrations for each of the base/neutral compounds which were identified are presented in Table 4-2. The minimum and maximum concentrations as the range and the number of determinations on which the average is based are also presented. A complete listing of the data obtained for each sample is given in the Appendix.

The total average amount of base/neutral extractable material measured by GC/MS is 96 mg/L or about 10 percent of the TCO material in the base/neutral fraction. The major portion of the TCO mass was phenolic material extracted into the base/neutral fraction. Approximately half of the non-phenolic compounds which were identified in the base/neutral fraction are EPA Appendix A Priority Pollutants. Thirty-five percent of the base/ neutral compounds identified are polynuclear aromatics which are all present at less than 10 mg/L. There are only four compounds identified in the base/neutral fraction which are present at concentrations greater than 10 mg/L. These compounds are:

- 2-Ethylpyridine
- Bis(2-ethylhexyl)phthalate
- Indole
- 2-Methylindole

These four compounds make up 56 percent by mass of the non-phenolic compounds identified in the base/neutral fraction.

TABLE 4-2. GC/MS ANALYSIS RESULTS OF EXTRACTED SEPARATOR LIQUOR BASE/NEUTRAL EXTRACTABLE COMPOUNDS

Compound	Concentration in the Liquor (mg/L) Average	Range	# of Identifications/ # of Determinations
TCO	1000	830 -1500	4/4
GRAV	360	290 - 440	6/6
†Naphthalene	8.6	1.6 - 17	6/6
†Acenaphthylene	3.6	1.2 - <6	6/6
†Fluorene	2.6	0.28 - <6	6/6
†Phenanthrene/Anthracene	2.3	0.7 - <6	6/6
†Fluoranthene	5.7	0.3 - <9	6/6
†Pyrene	5.7	0.4 - <9	6/6
†Bis(2-ethylhexyl)phthalate	12	1.2 - 32	6/6
†Chrysene	0.12		1/6
Benzo(b)fluoranthene	0.10		1/6
†Benzo(a)pyrene	0.12		1/6
Pyridine	1.2		1/6
2-Ethylpyridine	18	1.3 - 61	6/6
Quinoline	3.1	0.62 - 5.6	6/6
4-Methylquinoline	0.11		1/6
1-Methylnaphthalene	2.3	0.43 - 4.2	6/6
2,3-Dimethylnaphthalene	2.3	0.65 - <4.5	6/6
2,6-Dimethylnaphthalene	2.2	<1.3 - <3	5/6
Indole	12	8 - 14	6/6
2-Methylindole	12	2.2 - 16	5/6
3-Methylindole	2.4	0.58 - 3.6	6/6

†Appendix A Priority Pollutants

The bis(2-ethylhexyl)phthalate has the greatest variability of all of the base/neutral extractable compounds. At least part of this variability is probably due to contamination from a number of possible sources during sampling, extraction, and analysis. The compound with the least variability is the indole with a relative error of 18 percent, assuming a normal distribution.

Naphthalene was found to be the single polynuclear aromatic compound with the highest concentration of 8.6 mg/L with naphthalene derivatives contributing another 6.8 mg/L. The indoles represent the highest concentration as a group. The concentration of the indoles combined is 26 mg/L, with indole itself contributing 45.5 percent; 2-methylindole, 45.5 percent; and 3-methylindole, 9 percent.

4.1.4 Volatile Organic Compounds

Results of the volatile organic analysis (purgeable halocarbons and aromatics) are summarized in Table 4-3. Data for each sample are presented in the Appendix. The average concentration of benzene/toluene/xylene (BTX) is 1,300 mg/L. Of this concentration, benzene represents 47 percent; toluene, 32 percent; and total xylenes 21 percent of the total. The variability of the data for the volatile organic species over the sampling period is much lower than it is for the extractable organics. For samples collected on each of five consecutive days, the relative error of the concentration was 12 percent for benzene, 9 percent for toluene, and 17 percent for xylenes, assuming a normal distribution.

4.1.5 Mass of the Total Extractable Organics

The mass of total extractable organics was determined as the sum of the total chromatographable organics (TCO) and gravimetric analysis of residue after evaporation (GRAV). The TCO and GRAV data indicate an average total of 9,300 mg/L extractable organics for both acid and base/neutral extracts combined. Speciation by GC/MS identified an average total of 6,860 mg/L or 74 percent of the total extractable. The acid extract alone contained 7,900 mg/L extractable material with 3,260 mg/L or 41 percent identified by speciation. Table 4-4 summarizes the average TCO, GRAV, and total mass identified by GC/MS for the acid and base/neutral fraction as well as the total amount of material.

The GC/MS mass represents only the material actually identified in that fraction. The phenolic compounds which make up essentially all of the extractable organics are chromatographable and would be expected to be included in the TCO determination. The agreement between the total mass identified by GC/MS and the TCO value for the acidic compounds (which makeup the majority of the mass identified) support the validity of the concentration values obtained for the species present. In the acid extract, the

TABLE 4-3. GC/MS ANALYSIS RESULTS OF RAW SEPARATOR LIQUOR VOLATILE ORGANIC COMPOUNDS

Compound	Concentration (μg/L) Average	Range
† Benzene	630	560-740
† Toluene	420	380-460
† Ethylbenzene	48	22-106
m,p-Xylene	150	124-172
o-Xylene	280	34-184

† Appendix A Priority Pollutants

TABLE 4-4. MASS OF EXTRACTABLE ORGANIC MATERIAL IDENTIFIED IN EACH OF THE ABN EXTRACTS

	Acid	B/N	Total
TCO (mg/L)	2500	1010	3510
GRAV (mg/L)	5400	360	5760
$\sum$TCO + GRAV (mg/L)	7900	1370	9270
Total Mass Identified by GC/MS (mg/L)	3260	100* 3500†	6860

*Base/Neutral Extractable Compounds.
†Acid Extractable Compounds.

total mass identified by GC/MS is 3,260 mg/L, which is greater than the corresponding TCO of 2,500 mg/L. The average FID response of phenolic compounds relative to n-alkanes (which are used for TCO calibration) is about 75 percent. If, as indicated by GC/MS, essentially all of the TCO material were phenolic compounds, the measured TCO value would be 75 percent of the true concentration of chromatographable organics. If the TCO value of 2,500 mg/L for the acid extract is adjusted for this instrument response to assume all the material is phenolic in nature, the calculated TCO value for the acid extract becomes 3,330 mg/L. The total mass identified by GC/MS for the acid extract is 3,260 mg/L or 98 percent of the calculated TCO.

However, this rationale cannot explain the high amounts of phenolic compounds relative to the TCO in the base/neutral fraction. This discrepancy may be the result of the increased error attributable to analysis of these acid extractable compounds on the base/neutral GC column which results in relatively poor separation.

4.2 Sample Stability

4.2.1 Effect of Refrigeration

Table 4-5 shows the concentration of the acid and base/neutral extractable compounds for three extractions of the same sample over a period of one month. During the one month period, the aqueous sample was stored in amber bottles and maintained at 277 K (39°F).

Over the period, the gross amount of extractable material did not appear to change significantly as indicated by the consistency of TCO and GRAV values for each extraction. However, it does appear that the organic character of the sample changed. Over the month the total amount of material as determined by GC/MS decreased 55 percent. The compounds which demonstrated the greatest losses were substituted phenols. The phenol itself was fairly stable. Over the one month period, the concentration of phenol fell from 2,300 mg/L to 2,000 mg/L, or about 13 percent. The concentration of the methylphenols showed a 62 percent decrease over the first two weeks and an additional 19 percent decrease from the two week extraction to the one month extraction. The dimethylphenols demonstrated this drop even more dramatically. There was a 77 percent decrease in the concentration of dimethylphenols from Extraction I (initial) to Extraction II (two weeks) and 9 percent from Extraction II to Extraction III (one month). The concentration of the 2,4-dimethylphenol, a priority pollutant, fell 82 percent from Extraction I to II and 45 percent from II to III. Therefore, it would appear that the 2,4-dimethylphenol isomer degrades at a faster rate than the dimethylphenols in general. This is consistent with biological degradation data previously reported (Ref. 5).

TABLE 4-5. STABILITY STUDY RESULTS - STORAGE UNDER REFRIGERATION

Compound	Concentration (mg/L) First Ext'n. 9/05/80	Second Ext'n. 9/17/80	Third Ext'n. 10/01/80	Percent Remaining After One Month
TCO	3500	3400	3500	100
GRAV	5290	3770	4720	89
†Phenol	2300	2000	2000	87
Methylphenols	4200	1600	1300	31
Dimethylphenols (total)	1500	340	310	21
†2,4-Dimethylphenol	920	170	94	10
Trimethylphenol	<.35	<.32	<.27	
Indanol	<.07	<.07	1.0	NA
1-Naphthol	3.3	4.0	3.0	91
2-Naphthol		<.07	<.06	NA
Resorcinol/Catechol	3.6	Trace	14	NA
†Naphthalene	11	1.0	0.77	7
†Acenaphthalene	3.6	0.3	0.32	9
†Fluorene	<6	.05	.08	1
†Phenanthrene/Anthracene	1.3	.03	.14	10
†Fluoranthene	<9	<.1	<.1	
†Pyrene	<9	<.1	<.1	
†Bis(2-ethylhexyl)phthalate	22	0.15	0.26	1
2-Ethylpyridine	61	<0.05	<.05	<1
Quinoline	3.7	0.46	0.32	9
1-Methylnaphthalene	3.0	0.24	0.26	9
2,3-Dimethylnaphthalene	<4.5	<.05	<.05	
2,6-Dimethylnaphthalene	<3	0.04	0.1	
Indole	13.0	9.4	9.4	72
2-Methylindole	14	<.04	<.02	<1
3-Methylindole	2.6	<.02	<.02	<1

†-Appendix A Priority Pollutants
NA=Not Applicable

The base/neutral extractable compounds demonstrated a marked decrease in concentration over the first two weeks, generally by about one order of magnitude. However, from the two week extraction to the one month extraction, there was no appreciable change in concentration. The concentrations of naphthalene, acenaphthylene, and quinoline all decreased by about 90 percent, while the concentration of indole was the most stable of the base/neutral extractable compounds, dropping only about 30 percent over the one month period. No corresponding increases in the concentrations of any species which would indicate the formation of reaction and/or degradation products were observed.

4.2.2 Effect of Ambient Storage

Table 4-6 shows the results of successive analyses of separator liquor stored in an amber bottle at ambient temperatures. The concentration of most of the compounds identified decreases. The most noticeable difference is in the concentration of the phenol. After three weeks of storage at ambient temperatures, only 35 percent of the phenol remained. When stored at 277 K (39°F) for one month, 87 percent of the phenol remained. After three weeks of storage at ambient temperatures, the concentration of both the methyl- and dimethylphenols decreased by about 40 percent, contrasting with much larger decreases during cold storage.

The accelerated decomposition of the 2,4-dimethylphenol that was observed over a one month period in the refrigerated samples is again observed in the unrefrigerated sample. After 3 weeks of ambient storage, less than 45 percent of the 2,4-dimethylphenol remained while 64 percent of the total dimethylphenol remained. The phenols with a molecular weight greater than that of dimethylphenol (MW = 122) which appear fairly stable in the sample kept under refrigeration retain about 5 percent of their original concentration after ambient storage.

The base/neutral extractable compounds do not seem to be as affected by ambient storage as are the phenolic compounds. Their concentrations show a decrease with time, but with the low levels present, the difference could be in the range of the analytical variability.

No TCO was run for the control itself. The value presented represents the average concentration of three samples from the characterization study. The TCO for the sample kept at ambient conditions shows a slight increase over this average value. This sample was observed to have a darker color and increase in turbidity at the time of extraction. A greater degree of emulsion during extraction was also observed.

4.3 Comparison of Data from the Mobile GC/MS Program to Similar Data from Previous Studies

The data obtained from the Mobile GC/MS program are not the first to characterize the separator liquors. Previous studies have provided

TABLE 4-6. STABILITY STUDY RESULTS - STORAGE AT AMBIENT CONDITIONS

Compound	Concentration (mg/L) Control (9/13/80)	Three Weeks Later	Percent Material Remaining
TCO*	††3600(avg)	3988	
†Phenol	1900	670	35
Methylphenols	1500	880	59
Dimethylphenols (total)	330	210	64
† 2,4-Dimethylphenol	120	<54	<45
Trimethylphenol	2.2	<.12	<5.5
Indanol	1.2	<.05	<4.2
1-Naphthol	4.3	0.19	4.4
2-Naphthol	6.0	<.05	.83
Resorcinol/Catechol	20	<.38	1.9
†Naphthalene	1.6	1.0	63
†Acenaphthalene	1.5	0.73	49
†Fluorene	0.49	0.17	35
†Phenanthrene/Anthracene	0.70	0.43	61
†Fluoranthene	0.30	0.09	30
†Pyrene	0.40	0.06	15
†Bis(2-ethylhexyl)phthalate	1.4	0.14	10
†Chrysene	0.12	<.2	NA
Benzo(b)fluroanthene	0.10	<.14	NA
†Benzo(a)pyrene	0.12	<.14	NA
Pyridine	1.2	<.2	<17
2-Ethylpyridine	1.3	<.2	<15
1-Methylnaphthalene	.43	.6	NA
Quinoline	.62	.46	74
4-Methylquinoline	0.11	<.08	<73
2,3-Dimethylnaphthalene	.65	.55	85
Indole	8.0	4.1	51
3-Methylindole	1.4	<.05	<3.6

*No GRAV done on these samples.
†Appendix A Priority Pollutants.
††Average of TCO from 9/5, 9/7, 9/9.
NA=Not Applicable

information on wastewater samples from the same separator tank which were preserved and analyzed off-site. The results of two of these programs are presented in "The Chapman Addendum" (Ref. 6) and "Comparison of Coal Conversion Wastewaters" (Ref. 7). The "Chapman Addendum" presents the results of the first effort to characterize a low-Btu gasification facility, a program carried out late in 1977. "Comparison of Coal Conversion Wastewaters" presents the results of a study done in mid-1980 and concerns speciation of the organics in the separator liquor after exhaustive diisopropyl ether extraction. For comparison purposes, Table 4-7 presents a summary of the data obtained from each of the three programs. Data are presented for the extractable organics only. Complete speciation of every isomer was not achieved in any of these programs, consequently some compounds were determined as a group. The bracketed values represent a total concentration for all of the grouped isomers. During the Chapman Addendum work, two values were obtained for TCO and GRAV, one during a screening analysis and the other during the detailed analysis. The procedures used for each analysis are different, but the final results are comparable. Results of the volatile organic analyses are not included as these analyses were not attempted in previous programs.

While the TCO and GRAV values obtained in this program are consistent with previously reported values, the total estimated mass detected during this program is on the average approximately three times greater when compared to the "Chapman Addendum" data. The accountability is about twice as high as the "Coal Conversion Wastewater" data. For each compound identified in the "Chapman Addendum", the concentration is generally an order of magnitude lower than the corresponding concentration determined in the Mobile GC/MS program. The data contained in the "Coal Conversion Wastewater" paper addresses primarily phenolic compounds. The concentrations determined here are about half of that found during the mobile GC/MS program for phenol and methylphenols and about the same for dimethylphenols and naphthols. In the "Coal Conversion Wastewater" study, the ratio of phenol to methylphenol to dimethylphenol is approximately 1:1:1. The mobile GC/MS data show about twice as much phenol and three times as much methylphenols as the dimethylphenols. From comparison of these data and the information obtained from the degradation study in this program, it appears that the results obtained in the two previous programs may have suffered as a result of sample deterioration during shipment and storage and/or incomplete extraction of the water samples.

4.4 Physical Treatment of Separator Liquor

Tables 4-8 and 4-9 present the results of preliminary investigations into the removal of organics by diisopropyl ether extraction and by wet oxidation.

The DIPE extraction procedure used for this study was designed to have 2.6 theoretical stages and, thus, duplicate the 99.5 percent phenol removal achieved by the Lurgi Phenosolvan process. The observed phenol

TABLE 4-7. COMPARISON OF MOBILE GC/MS DATA WITH DATA FROM OTHER WASTEWATER STUDIES AT THE SAME SITE

(concentrations given in mg/L in separator liquor)

Parameter	Mobile[1] GC/MS	Chapman[2] Addendum	Comparison[3] of Coal Conversion Wastewaters
Estimated total mass detected	3.8E3 to 9.5E3† 6.86E3 Avg.	2.46E3	4.12E3*
TCO and GRAV	9.27E3	4.86E3 (screening analysis) 1.1E4 (detailed analysis)	
Phenol	2.4E3	6E2	1.5E3
o-Cresol	3.2E3	1E3	4.2E2
m and p-Cresol			1.1E3
Total DMP	1.2E3		1.1E3
2,6-Dimethylphenol	4.2E2		1.9E1
2,4-Dimethylphenol			2.0E2
3,5-Dimethylphenol			1.7E2
3,4-Dimethylphenol			6.8E2
1-Naphthol	5.0E0	1E0	1.5E1
2-Naphthol	6.7E0		
Indanol	1.7E0		
Naphthalene	8.6E0	8E-1	
Methylnaphthalenes	2.3E0	4E-1	
Acenaphthylene	3.6E0	4E-1	
Indole	1.2E1	2E0	
2-Methylindole	1.2E1	4E-1	
3-Methylindole	2.4E0		
Quinoline	3.1E0	2E-1	1.0E1

aEb = a x 10^b

†Range of values obtained for 6 sets of data

*Value reported is sum of the available concentrations.

[1]Samples extracted on site using $CH_2Cl_2/(C_2H_5)_2O$.

[2]Samples extracted on site using CH_2Cl_2.

[3]Samples preserved in amber bottles at 4°C and extracted within 10 days of sample collection using diisopropyl ether.

TABLE 4-8. EFFICIENCY OF ORGANIC COMPOUND REMOVAL FROM SEPARATOR LIQUOR BY DIPE EXTRACTION

Compound	Concentration in Liquor (mg/L) Control (9/13/80)	After DIPE Extraction	% Removal Efficiency from Control Sample
TCO	3600*	326	91
GRAV	4300	1300	70
Phenol	1900	21	99
Methylphenols	1500	17	99
Dimethylphenols	330	12	96
2,4-Dimethylphenol	120	ND	
Trimethylphenol	2.2	ND	
Indanol	1.2	ND	
1-Naphthol	4.3	ND	
2-Naphthol	6.0	ND	
Resorcinol/Catechol	20	ND	
Hydroxybenzaldehyde	<.3	ND	
Naphthalene	1.6	ND	
Acenaphthylene	1.5	ND	
Fluorene	0.49	ND	
Phenanthrene/Anthracene	0.70	ND	
Fluoranthene	0.3	ND	
Pyrene	0.4	ND	
Bis(2-ethylhexyl)phthalate	1.4	1.4	0
Chrysene	0.12	ND	
Benzo(b)fluoranthene	0.10	ND	
Benzo(a)pyrene	0.12	ND	
Pyridine	1.2	ND	
2-Ethylpyridine	1.3	ND	
Quinoline	0.62	ND	
4-Methylquinoline	0.11	ND	
1-Methylnaphthalene	0.43	ND	
2,3-Dimethylnaphthalene	0.65	ND	
Indole	8.0	ND	
3-Methylindole	1.4	ND	
Diethylphthalate	ND	.38	

*Average of three samples from 100-hr. monitoring.
ND=Not Detected

TABLE 4-9. EFFICIENCY OF ORGANIC COMPOUND REMOVAL FROM SEPARATOR LIQUOR BY WET OXIDATION

Compound	Resistance to Biodegradation†	Concentration (mg/L) Control (9/13/80)	After Wet Oxidation	% Removal Efficiency from Control Sample
TCO		3600*	250	93
GRAV		4300	350	92
Phenol	E	1900	280	85
Methylphenols	E	1500	80	95
Dimethylphenols	E/R	330	12	96
2,4-Dimethylphenol	NR	120	<2.8	>98
Trimethylphenol	M/R	2.2	<0.63	>71
Indanol	R	1.2	<0.27	>78
1-Naphthol	M	4.3	<0.63	>85
2-Naphthol	E	6.0	<0.27	>96
Resorcinol/Catechol	E	20	<2.0	>90
Hydroxybenzaldehyde	E/M	<.3	2.2	>90
Naphthalene	E	1.6	<1	>38
Acenaphthylene	NR	1.5	1.0	33
Fluorene	NR	0.49	<2	NA
Phenanthrene/Anthracene	NR	0.70	<2	NA
Fluoranthene	NR	0.3	<3	NA
Pyrene	NR	0.4	<3	NA
Bis(2-ethylhexyl)phthalate	NR	1.4	0.34	76
Chrysene	NR	0.12	<1	NA
Benzo(b)fluoranthene	NR	0.10	<1.6	NA
Benzo(a)pyrene	NR	0.12	<1	NA
Pyridine	R	1.2	<1	NA
2-Ethylpyridine	R	1.3	<1.7	NA
Quinoline	E	0.62	<1.1	NA
4-Methylquinoline	R	0.11	<1.1	NA
1-Methylnaphthalene	E	0.43	<1.2	NA
2,3-Dimethylnaphthalene	R	0.65	<1.6	NA
Indole	M	8.0	<3.4	>58
3-Methylindole	E	1.4	<1	>29

*Average of three samples from 100-hr. monitoring.
†Ref. 5
E = Easily Degraded
M = Moderately Degraded
R = Resistant to Degradation
NR = Biodegradation data not reported.
NA = Not Applicable.

removal efficiency for phenols using this procedure was 99 percent as was the removal efficiency for methylphenol. The removal efficiencies for phenolic compounds with molecular weights greater than that of methylphenol were significant but could not be quantitatively defined because these compounds were not detectable in the extracted water. The concentration of the phthalates found in the base/neutral extractable fraction did not change. The DIPE extraction removed about 91 percent of the TCO material and 70 percent of the GRAV material from the water. Total phenolic compounds were reduced by two orders of magnitude.

Wet oxidation removes almost as much of the phenolic compounds as the DIPE extraction. After the water was treated and analyzed, it was found that 85 percent of the phenol, 95 percent of the methylphenols, and 96 percent of the dimethylphenols were removed by wet oxidation. At least 40 percent of the naphthalene, 60 percent of the indole, and 30 percent of the acenaphthylene were also removed. After oxidation, 93 percent of the TCO material and 92 percent of the GRAV material was removed. During ambient storage, the concentrations of the phenolic materials also show a marked decrease, however, the concentration of the total amount of organic extractable material remains unchanged as indicated by the stable TCO value.

Wet oxidation may be applicable in the treatment of streams which contain organic compounds which are not easily biodegradable. Table 4-9 also lists some of the compounds, their resistance to biodegradation (Ref. 5) and their concentrations before and after wet oxidation treatment. Some of the compounds have isomers which are both moderately and easily degraded and, therefore, are given two designations for their resistance.

The overall feasibility of water treatment using the wet oxidation method is limited. Its ability to remove organic material is almost as great as the DIPE extraction but has not found wide commercial application due to the generally high cost associated with the treatment. To date, its usefulness is limited to a few specific applications where there is a need for treatment of highly toxic and/or organic laden streams from small facilities.

SECTION 5

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APPENDIX A

TABLE A-1. CARRYOVER OF PHENOLS INTO THE B/N EXTRACT

Compound(mg/L)	9/5/80	9/6/80	9/7/80	9/8/80	9/9/80	9/13/80
PHENOL						
Acid	1900	2200	1600	1800	1800	1800
B/N	370	590	1800	470	120	100
Total	2300	2800	3400	2300	1900	1900
B/N % of Total	16	21	53	20	6	5
METHYLPHENOLS						
Acid	1800	1500	690	1200	900	1100
B/N	2400	3200	30000	2900	580	430
Total	4200	4700	30700	4100	1500	1500
B/N % of Total	57	68	98	71	39	29
DIMETHYLPHENOLS						
Acid	230	400	44	120	130	81
B/N	1300	1300	1900	1100	220	250
Total	1500	1700	1940	1200	350	330
B/N % of Total	87	76	98	92	63	76

TABLE A-2. CHARACTERIZATION STUDY: ACID EXTRACTS (mg/L)

Compounds	09/05/80	09/06/80	09/07/80	09/08/80	09/09/80	09/13/80
Dimethylphenol	5.5	<0.2	<0.6	<0.6	<0.42	<0.12
Phenol	1900	2200	1600	1800	1800	1800
Methylphenols	530	420	190	340	350	220
2,4-Dimethylphenol	140	190	5.7	32	36	30
Dimethylphenol	58	190	32	64	74	42
Dimethylphenol	27	25	6.6	2.2	20	8.9
Trimethylphenol	<0.17	<0.12	<0.35	<0.35	<0.25	2.2
Indanol	<0.07	2.0	0.74	3.2	2.8	1.2
Hydroxybenzaldehyde	<0.3	<0.18	19	<0.57	14	<0.3
1-Naphthol	3.3	ND	3.4	8.5	5.6	4.3
2-Naphthol	ND	ND	5.4	9.2	6.0	6.0
Resorcinol/Catechol	3.6	ND	65	20	40	20
Methylphenol	1300	1100	500	810	550	830
Pentafluorophenol (Spike @ 100 mg/L in the acid extract.)	15	25	26	22	21	22

ND = Not Detected

TABLE A-3. CHARACTERIZATION STUDY: BASE/NEUTRAL EXTRACTS (mg/L)

Compound	09/05/80	09/06/80	09/07/80	09/08/80	09/09/80	09/13/80
Pyridine						1.2
2-Ethylpyridine	61	34	<4	<2.1	4.7	1.3
Naphthalene	11	9.4	17	11	1.7	1.6
1-Methylnaphthalene	3.0	2.1	4.2	3.3	0.48	0.43
Quinoline	3.7	<3.3	5.6	4.3	0.78	0.62
2,3-Dimethylnaphthalene	<4.5	<4.5	1.2	1.2	<2	0.65
2,6-Dimethylnaphthalene	<3	<3	<2.5	<1.3	<1.4	ND
Indole	13.0	12	14	11	13	8.0
4-Methylquinoline	ND	ND	ND	ND	ND	0.11
3-Methylindole	2.6	2.9	3.6	3.6	0.58	1.4
2-Methylindole	14	14	16	12	2.2	ND
Acenaphthylene	3.6	<6	5.3	4.0	1.2	1.5
Fluorene	<6	<6	1.6	1.1	0.28	0.49
Anthracene/Phenanthrene	1.3	<6	2.7	1.8	1.2	0.70
Fluoranthene	<9	<9	<7.5	<4.2	<0.1	0.30
Pyrene	<9	<9	<7.5	<4.2	<4.2	0.40
Bis(2-ethylhexyl)phthalate	22	32	11	1.2	1.9	1.4
Chrysene	ND	ND	ND	ND	ND	0.12
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	0.10
Benzo(a)pyrene	ND	ND	ND	ND	ND	0.12

ND = Not Detected

TABLE A-4. CHARACTERIZATION STUDY: VOLATILE ORGANIC COMPOUNDS (μg/L)

	09/05/80	09/06/80	09/07/80	09/08/80	09/09/80
Benzene	640	560	640	560	740
Toluene	460	380	440	380	440
Ethylbenzene	30	106	42	22	42
m,p-Xylene	168	132	124	142	172
o-Xylene	184	34	166	116	146
Total Xylenes	352	166	290	258	318